Final Report

National Aeronautics and Space Administration

Grant No. NAG-1-600

INNOVATIVE METHODS FOR THE MEASUREMENT OF I* QUANTUM YIELDS AND KINETICS BY DIODE LASER GAIN-VERSUS-ABSORPTION

Report Period: 1 July 1985 - 30 June 1987

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Research has been performed to investigate new methods for determination of quantum yields and kinetics of excited $I^*(^2P_{1/2})$ atoms, some of which are relevant to solar-pumped lasers. A new diode laser technique was developed to probe I and I^* atoms at 1315 nm using the method of laser gain-versus-absorption. This method was shown to be highly accurate, versatile, and powerful.

Work in progress was also performed using an older technique, infrared emission, to characterize the quantum yields of a large variety of solar lasant candidate molecules. Most of these molecules were synthesized by Professor Christopher Shiner and his research group, while a few molecules were provided by NASA personnel for testing.

Publications

This work has resulted in the following publications:

1. H.K. Haugen, E. Weitz, and S.R. Leone, "Accurate quantum yields by laser gain vs. absorption spectroscopy: Investigation of Br/Br* channels in photofragmentation of Br_2 and IBr," J. Chem. Phys. 83, 3402 (1985).

2. H.K. Haugen, E. Weitz, and S.R. Leone, "Effect of spin-orbit excitation on reactivity: Laser transient absorption spectroscopy of $Br(^2P_{1/2}, ^2P_{3/2})$ + IBr reactive dynamics," Chem. Phys. Lett. 119, 75 (1985).

3. W.P. Hess, S. Kohler, H.K. Haugen, and S.R. Leone, "Application of an InGaAsP diode laser to probe photodissociation dynamics: I^* quantum yields from n- and i-C_3F_7I and CH_3I by laser gain vs. absorption spectroscopy," J. Chem. Phys. 84, 2143 (1986).

4. W.P. Hess and S.R. Leone, "Absolute I^* quantum yields for the ICN A state by diode laser gain vs. absorption spectroscopy," J. Chem. Phys. 86, 3773 (1987).

5. J.E. Smedley, W.P. Hess, H.K. Haugen, and S.R. Leone, "Transient gain-versus-absorption laser probing of spin-orbit states, kinetics, and dynamics," J. Chim. Phys. (in press).

Brief Summary of Accomplishments

(A) Quantum Yields of Solar Laser Candidates

The quantum yields of a large variety of candidate molecules for solar lasant materials to produce I^* were tested. The absorption spectrum was measured for each compound and the I^* yield determined by the diode laser or by infrared emission, using C_3F_7I as a standard. The results of these measurements are summarized in Table I.

It can be seen from the table that a wide range of materials was tested, including novel metal complexes and numerous organic compounds which were synthesized by the Shiner group in an attempt to shift the wavelength of the ultraviolet absorption to longer values. None of the new compounds offer any significant improvement over the best known candidates, n- and i-C_3F_7I and t-butyl-C_4F_9I. Reliable yield data was obtained on these "standard" compounds as well.

(B) Development of Diode Laser Probing of I/I^*

A GaAsInP diode laser system was developed to probe I and I^* atoms to obtain yields and kinetics. A new technique of gain-versus-absorption spectroscopy was pioneered to measure quantum yields with high accuracy. The technique was applied to several standard compounds, n- and i-C_3F_7I to provide definitive information on these yields. The errors in the yield data were reduced to $\pm 2\%$ or less. The standard compounds were shown to have yields of 100% to within these error bars.

In addition, a detailed study of the yield of I^* from ICN as a function of dissociation wavelength was completed (Table II).

All of the details of the diode laser tuning and operation and the results of these studies have been described thoroughly in previous reports and in the publications.

(C) Narrow Line Operation of the Diode Laser

New work is being carried out to apply a recently discovered method of locking the diode laser to a Fabry Perot cavity (due to Leo Hollberg, NBS, private communication). Recent progress has been made to lock our diode lasers by feedback from an external, high-Q Fabry Perot resonator. The resulting narrow line output will be used to probe Doppler line profiles in I^* media.

The results of this work will acknowledge NASA support when it is completed and published.

(D) Hyperfine State-Changing Rates

A new experiment has been set up to measure the rates of F-sublevel changing collisions in both the I ground state and the I^* excited state. Theory predicts that the cross sections to mix F=2,3 in the upper state should be very slow, whereas the collisional mixing of F=1,2,3,4 in the ground state should be fast. A three laser experiment has been devised to measure these processes directly.

A pulsed ultraviolet laser will dissociate C_3F_7I to produce I^* with 100% yield. A second pulsed, Raman shifted dye laser at 1315 nm will then "dump" some population out of the upper hyperfine levels (F=2 or 3). The diode laser will then probe the repopulation kinetics of the fast mixing in the ground state and the slow collisional transfer in the excited state.

The results of this work will also acknowledge NASA support when it is completed and published.

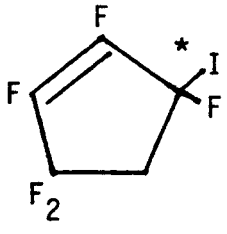
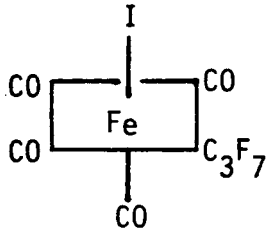
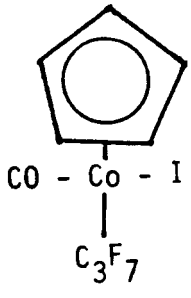
(E) Recombination Kinetics

Experiments and modelling were carried out to explore the possibility of measuring the recombination rates of I^* with C_3F_7 radicals. Although the computer models indicated that such observations should be possible, the

experiments were never able to monitor the correct effects. Possibly laser multiphoton processes begin to interfere at the power densities that are necessary to observe the radical recombination effects.

The details of the kinetic model and the expected signals showed that a combination of IR fluorescence and simultaneous diode laser probing can offer a powerful means to elucidate the fraction of I^* atoms that recombine, rather than quench. The total rates of removal of I^* by the radical collisions can be extracted by observing the enhanced disappearance of the I^* atoms in the presence of the radicals. The form of this kinetics has been worked out in detail.

Table I. I^* Yields from Solar Lasant Candidate Molecules.

Compound	Φ_I^* (%) (@ 266 nm unless noted)	λ_{max} (nm)	Quenching $cm^3 \cdot molec^{-1} \cdot s^{-1}$	Method
$n\text{-}C_3F_7I$	100 ± 4	272	10^{-16}	IR + diode
$i\text{-}C_3F_7I$	100 ± 7	273	10^{-16}	IR + diode
$n\text{-}C_4F_9I$	95 ± 5	272	10^{-16}	IR
	100 ± 5 (278 nm)			
	100 ± 5 (292 nm)			
$t\text{-}C_4F_9I$	100 ± 7	290	--	diode
$F_2C{=}CFCF_2I^*$	63 ± 5	273	5×10^{-14}	IR
	60 ± 5 (303 nm)			
	45 ± 5	250	5×10^{-14}	IR
CH_3I	73 ± 4	270	1.7×10^{-12}	diode
	70 ± 7 (193 nm)			
BI_3	130 ± 11†	347	1.5×10^{-10}	IR
$(CF_3)_3Ge\text{-}I$	30 ± 5	235	10^{-14}	IR
$(CF_3)_3Ti\text{-}I^*$	53 ± 5	298	4.2×10^{-13}	IR
	--	400		IR
	This compound was photolyzed in 3 absorption bands at 418 nm, 323 nm and 266 nm. All three wavelengths produce vibrationally excited CO. No I^* was observed. No I ground state was observed by the diode either.			
		410		
	This compound is of low vapor pressure and it decomposes upon heating			

* Purity is suspect.
† Multiphoton process.

Table II. Diode Laser Gain vs Absorption Quantum Yields for ICN.

λ(nm)	Φ_I*(%)
284	53 ± 2
280	58 ± 2
276	63 ± 2
272	65 ± 4
266	66 ± 2
260	63 ± 3
248	44 ± 4